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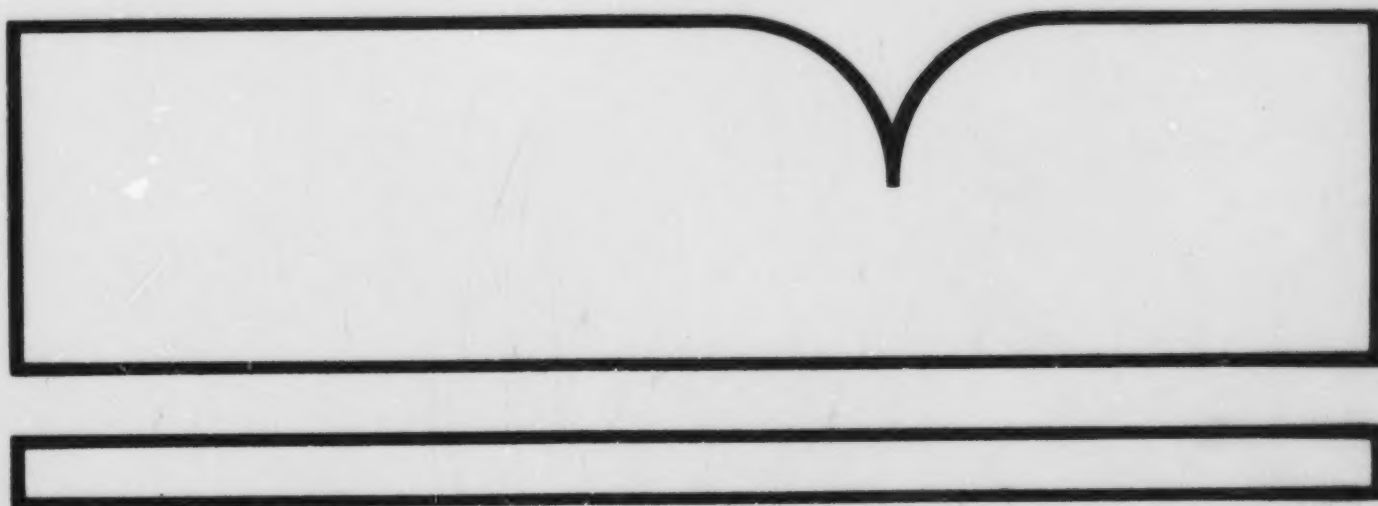
Testing and Evaluation of an Alcohol Production
Facility Utilizing Potatoes as a Feedstock

Acurex Corp., Mountain View, CA

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TESTING AND EVALUATION OF AN ALCOHOL PRODUCTION FACILITY
UTILIZING POTATOES AS A FEEDSTOCK

by

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16. ABSTRACT This study presents the sampling and analysis results for the characterization of liquid effluents and solid residuals from a culled potato feedstock process for the production of ethanol for use as fuel. The facility tested produces approximately 1 million gallons per year of ethanol and is located in eastern Idaho. Liquid and solid samples were taken throughout the process from the following locations: sluice/flume water, chopper product, makeup water, cooker product, fermenter product, beer tank, stillage, interim and final product, washwater, fusel oil, bath and "Sparkle" bath. Analytical results for the ethanol plant effluents include: ethanol and sugar content, conventional parameters, metals, cyanide, phenols, nutrients, oil and grease, priority pollutant organics, and selected pesticides. The most significant characteristics of concern were the BOD and COD levels. The cooker product and fermenter product samples showed the highest levels; 105,000 mg/L for BOD and 210,000 mg/L for COD. All streams exhibited pH 5, high TOC (1600 to 57,500 mg/liter) and high TSS (up to 35,000 mg/liter). The metals detected in levels over 100 ug/liter include Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Hg, Ti, and Zn. In the excess stillage, magnesium was 176,000 ug/liter and Calcium was 140,000 ug/liter).		
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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the regulated pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes an environmental evaluation of fuel alcohol production using culled potatoes as feedstock. The study was conducted to acquire basic information on the amount and type of pollutants generated by such units. This information will be used by the Regional Offices and Program Offices in determining the need for regulatory action in this area.

Further information concerning alcohol fuels can be obtained from the Director, IERL-Ci's, Energy Pollution Control Division.

David C. Stephan
Director
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Cincinnati

ABSTRACT

The U.S. Environmental Protection Agency (EPA) has conducted a study of the fuel alcohol industry to determine the environmental impact of alcohol fuel production from grain and waste products. As part of these studies, several grain and waste-product feedstock facilities have been examined.

Many of the newer facilities incorporate feedstocks such as sugar beets, culled potatoes and fruit, and sweet sorghum rather than the grain and waste products analyzed in the past. This study presents the sampling and analyses results of the liquid effluents and solid residuals from an ethanol production facility, located in eastern Idaho, which produces approximately 1 million gal/yr of ethanol using culled potatoes as a feedstock. The effluents were sampled in December 1981 and analyzed by Acurex Corporation under contract 68-03-3043 for EPA.

Liquid and solid samples of various process and effluent streams including the feedstock, make-up water, distillation feed, byproduct, beer bottoms, product, and washout water were analyzed in the laboratory for priority pollutants, metals, herbicides and pesticides, and other standard chemical analysis (e.g., biochemical oxygen demand, chemical oxygen demand). The most significant result was the identification of very high biochemical oxygen demand (up to 105,000 mg/L), chemical oxygen demand (up to 210,000 mg/L), total organic carbon (up to 57,500 mg/L), and total suspended solids levels (up to 35,000 mg/L) in both process and waste streams. The streams were also acidic (i.e., pH less than 5). The levels of priority pollutants were below current promulgated Resource Conservation and Recovery Act Standards, but some metals exceeded state standards.

Several recommendations, including ponding and acid neutralization of the effluent are presented to minimize the impacts.

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SECTION 1

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) conducted a study of the fuel alcohol industry to determine the environmental impact of alcohol fuel production from grain and waste product. As part of this study, the Industrial and Environmental Research Laboratory in Cincinnati, Ohio (IERL-CI) and the Effluent Guidelines Division (EGD) conducted sampling and analyses to characterize the air, water, and solid waste streams from alcohol facilities and obtain treatability information. Since many of the newer facilities incorporate other feedstocks such as sugar beets, culled potatoes and fruit, and sweet sorghum rather than the grain and waste product feedstocks analyzed in the past, EPA has begun to evaluate the environmental impacts of these nongrain feedstock facilities. This study presents the sampling and analyses of the liquid effluents and solid residuals from an ethanol production process which uses one of the above feedstocks -- potatoes.

The facility tested, located in eastern Idaho, produces approximately 1 million gal/yr of ethanol using culled potatoes as feedstock. The effluents were sampled in December 1981 and analyzed by Acurex Corporation under contract 68-03-3043 for EPA. This report describes the results of this study. Section 2 of this report describes the process at the facility; Section 3 presents the techniques used to acquire the samples for analysis; Section 4 outlines the analytical techniques employed; and Section 5 presents results and the environmental impact associated with the effluents. Appendix A contains the quality assurance and control (QA/QC) results.

SECTION 2

PROCESS DESCRIPTION

The alcohol production facility, shown in Figure 1, converts potatoes and grains into ethanol. During the sampling period of December 2, 3, and 4, 1981, potatoes were used as the feedstock. A flow diagram of the alcohol production processes through the production of the "beer" is illustrated in Figure 2.

Culled potatoes arrive at the plant by truck and are placed in a storage shed. When needed, they are transported by flume and conveyed to a grind mill located on top of the batch process tank. The potatoes are relatively clean when delivered to the plant, but dirt is removed as they are conveyed by water in the flume. The flume water is recirculated for approximately 3 days and then disposed of in an onsite wastewater lagoon.

The milled potatoes are transferred from the batch tank to the cooker by a screw conveyor and pump. Both methods of transfer are necessary because the ground potatoes tend to separate into a high solids layer and a homogenized liquid fraction. Since the bulk of the potato feedstock consists of water, no additional water is needed except that introduced through condensation of the live steam injected in the cooking step. Cooking and fermentation are accomplished in a batch manner with approximately 85,300 lb of potatoes processed in each batch. Full operation calls for processing five batches over a 3-day period. The plant operates 24 hr a day.

The cook sequence is initiated by filling the single cooker with milled feedstock and adding 5 gal of carbohydrase enzyme (Taka-Therm), 9.7 lb of epsom salt, and 14 lb of lime. The pH is checked and adjusted with lime to between 6.0 and 6.5. The slurry is then heated with live steam to 196°F and held at this temperature for roughly 1 hr while being continuously agitated. An estimated 11,040 lb of live steam is added per batch.

During the cooking period, the starches are converted to complex sugars called dextrans. When dextrification is complete as indicated by a simple iodine test to measure the quantity of starch remaining, the slurry pH is adjusted to between 4.0 and 4.5 with sulfuric acid. When this is achieved, cooling is initiated by circulating the slurry through the shell-and-tube heat exchanger. This cooling step requires approximately 65 to 75 min.

When a batch temperature of 138°F is reached, 5 gal of glucosylase enzyme (Diazyme) is added to promote breakdown of dextrans into simple sugars. in each batch. Full operation calls for processing five batches

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north

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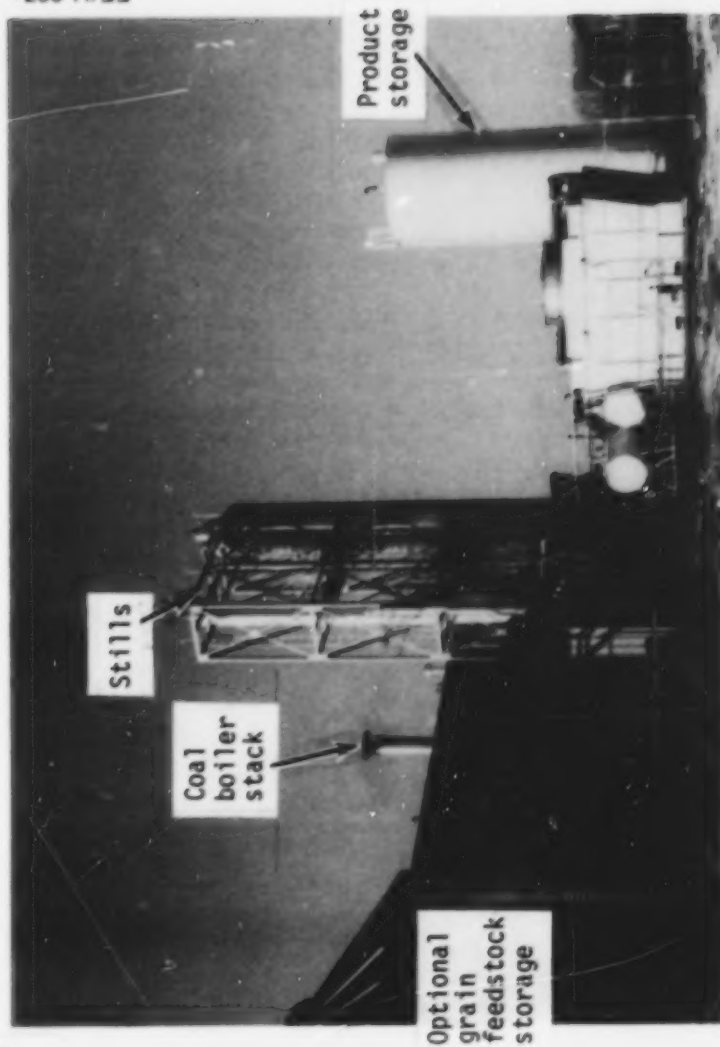


Figure 1. Alcohol production facility.

over a 3-day This step requires 2 to 3 hr, after which time the pH is adjusted to 5.0 by adding sodium hydroxide. After this adjustment is made, the cooker slurry is cooled to 96°F as it is transferred to one of three fermentation tanks. Again, cooling is achieved by passing the slurry through a shell-and-tube heat exchanger. The heat load is absorbed by cooling water circulated through a forced-draft cooling tower.

Fermentation for each batch is handled in one of three stainless steel tanks. Each tank is equipped with agitators and cooling coils that are connected to the circulating cooling water system. As the cooker slurry is being transferred to a fermenter and the agitator level is reached, 35 lb of yeast (Red Star Distillers Active Dry Yeast), 2 qt of antifoam, and 0.3 lb of zinc sulfate are added. Fermentation is carried out at 96°F and generally requires 30 to 36 hr. At this point the fermentation mash contains approximately 8 percent ethanol. Fermented mash is transferred to a "beer" tank for interim storage prior to distillation.

The cooking and fermentation sequences for the batches processed during the sampling period are tabulated in Table 1. Pertinent process parameters and batch makeup constituents are summarized in Table 2.

After each batch is cooked or fermented and the specific process tank is emptied, it is cleaned and sterilized. The cleaning and sterilization process involves a five-step sequence of three rinse cycles and two chemical wash cycles. The initial step used about 700 gal of well water to rinse residual amounts of slurry from the cooker or fermenter. The first portion of this rinse water is then sent to either the fermenter or beer storage tank with the remaining portion being disposed of in the wastewater lagoon. This initial rinse is followed by a caustic wash (35 lb of "Sparkle" per 500 gal) which is returned to the makeup tank and reused for about 6 days. A second rinse with 700 gal of fresh water then follows with the spent rinse water being discharged to the lagoon. The process unit is then washed with a dilute acid solution (1 gal of 75 percent H_3PO_4 solution per 500 gal). As in the case of the caustic wash solution, the acid wash solution is returned to its makeup tank after each use and reused until it is spent (about 6 days). This entire sequence ends with a final rinse cycle. Seven hundred gal of chlorinated fresh water are used and discharged to the wastewater lagoon when the cycle is completed.

This plant is equipped with a continuously operating still for producing 190-proof ethanol followed by a benzene dehydration system. Three 40-ft by 24-in diameter columns serve as the beer still, rectifying column, and dehydration column. The process flow diagram for these systems is illustrated in Figure 3.

Fermented mash from the beer storage tank is continuously pumped through a heat exchanger into the stripping column (beer still) at an average rate of 800 gal/hr. Live steam is injected into the bottom of the stripping column at a rate of 1,350 lb/hr to maintain a stripper bottom temperature of 210°F. The feed temperature averages 135° to 140°F. After passing through the beer still, the uncondensed vapors are passed through an entrainment separator

TABLE 1. COOKING AND FERMENTATION CHRONOLOGY

	Batch no. 26		Batch no. 27		Batch no. 29 ^a	
	Date	Time	Date	Time	Date	Time
Grind starts	11/29	2230	12/1	0535	12/2	0930
Grind stops	12/1	0305	12/1	1700	12/2	1830
Cooker charge starts	12/1	0305	12/1	1729	12/2	1830
Enzyme tanks filled	11/30	2100	12/1	--	12/2	1215
Agitator level reached	12/1	0411	12/1	1908	12/2	2215
Taka-Therm added	12/1	0411	12/1	1908	12/3	0108
Epsom salts added	12/1	0405	12/1	1930	12/3	0108
Lime added	12/1	0405	12/1	1930	12/3	0110
Charge completed	12/1	0513	12/1	--	12/3	0300
Batch tank cleaned	12/1	0533	--	--	12/3	0220
Cooker reached 196°F	12/1	0906	12/2	2415	12/3	0530
Dextrification complete	12/1	1006	12/2	0100	12/3	0615
pH changed to 4.0 to 4.5	12/1	1030	12/2	0125	12/3	0700
Cooling started	12/1	1010	12/2	0105	12/3	0620
Cooker reached 138°F	12/1	1115	12/2	0221	12/3	0732
Difazyme added	12/1	1120	12/2	0221	12/3	0732
Saccharification complete	12/1	--	--	--	12/3	0937
pH changed to 5.0	12/1	1410	12/2	0438	12/3	--
Sample taken	12/1	1410	12/2	0534	12/3	--
Pump to fermenter	12/1	1410	12/2	0445	12/3	0950
Agitator level reached	12/1	--	12/2	0530	12/3	1000
Yeast added, antifoam added	12/1	1500	12/2	0530	12/3	1000
Fermenter full	12/1	1545	12/2	0625	12/3	1120
Cooker cleaned	12/1	1630	--	--	12/3	1130
Fermentation complete	12/2	2245	--	--	12/3	--
Transfer to beer tank -- start	12/2	2300	12/3	1635	12/3	--
Transfer to beer tank -- stop	12/2	--	--	--	12/3	--
Fermenter cleaned	12/2	--	--	--	12/3	--

^aBatch no. 29 was started during test period but was incomplete at the time of the test termination

TABLE 2. PROCESS DATA

	Batch no. 26	Batch no. 27	Batch no. 29 ^a
Batch weight	85,300	86,300	86,300
Taka-Therm added (gal)	5	5	5
Epsom salts added (lb)	9.7	9.7	9.7
Lime added (lb)	14	14	14
pH at start of cook	6.0	6.0	5.9
Time at 196°F (hr:min)	1:04	0:50	0:50
Diazyme added (gal)	5	5	5
Time at 138°F (hr:min)	2:55	2:41	2:18
Yeast added (lb)	35	35	35
Antifoam added (qt)	2	2	2
Zinc sulfate added (lb)	0.3	0.3	0.3
Fermentation length (hr:min)	32:00	34:10	--

^aBatch no. 29 was started during test period but was incomplete at the time of the test termination

into a rectifying column. The rectifier bottom, middle, and top temperatures were measured and averaged 191°, 162°, and 154°F, respectively, during the sampling period. These temperatures are controlled by varying the reflux flow (i.e., pumping a portion of the condensed product back to the top of the column) which ranges from 0 to 500 gal/hr. The vapors from the rectifier are condensed in a water-cooled condenser and either recycled as reflux or sent to the 190-proof interim product storage tank. During the sampling period, approximately 60 gal/hr of 190- to 197-proof ethanol were produced.

Stillage is continuously removed from the beer still through a float tank and then separated into "thick" and "thin" streams. This flow is not measured but is estimated at 885 gal/hr at 5 percent solids for a design beer feed rate of 800 gal/hr to the still. The stillage dewatering device is designed to concentrate the stillage solids to a level of approximately 10 to 12 percent. This stream is then conveyed to a truck and hauled away for use as cattle feed. Approximately 11,200 lb of this thick stillage are produced daily. The thin stillage is discharged to an onsite lagoon. During the December sampling period, a fraction of the stillage could not be handled by the dewatering device and was also discharged into the lagoon.

Fusel oils are distilled from the ethanol and removed as a side stream from the rectifying column. A mixture of these oils and similar boiling point compounds are drawn from the rectifying column at a rate of approximately 10 gal/hr, cooled, mixed with fresh water, and sent to the fusel oil decanter. The separated fusel oil layer is discarded (volume estimated at 1 to 4 gal/day) and the decanter bottoms are pumped back to the rectifying column.

The plant also features a complete ethanol dehydration process consisting of a dehydrating column, decanter, recovery column, and associated pumps and tanks. Benzene is used as the dehydrating agent. During the December sampling period, this portion of the process was experiencing operating difficulties and complete dehydration was not achieved. Since benzene dehydration of ethanol has been studied in previous EPA programs, this process was not sampled during this study.

During the testing period two batches were completed and a third started, as shown in Table 1. Since this plant had only recently gone onstream, careful procedures were adhered to in order to demonstrate performance. Attention was not being given to optimize production parameters at this time. The operation tests indicated that the batches sampled were produced within performance guidelines set forth by the plant designers/constructors; thus, the results should represent normal operation with the exception of the previously discussed problems with the dehydration section.

SECTION 3

SAMPLING TECHNIQUES

The purpose of the sampling effort at this ethanol production facility was to characterize solid and liquid discharges and potential (i.e., during abnormal operation) discharge streams throughout the process. Based on the results of previous studies (1,2), gaseous emissions were not included in this study. The following paragraphs discuss the solid and liquid sampling techniques used during the December sampling period.

Liquid and solid samples were taken throughout the process from the following locations:

- Sluice/flume water
- Chopper product
- Makeup water
- Cooker product
- Fermenter product (two types)
- Beer tank (two types)
- Stillage (three types)
- Interim product (190 proof)
- Final product (200 proof)*
- Cooker washout
- Fermenter washout
- Fusel oil

*Since the dehydration unit was not operating during the sampling period, a final product sample was obtained at a later date.

- Acid bath
- Sparkle bath

Table 3 lists these samples, the type of sample, their respective sampling point, and the locations as designated in Figures 2 and 3. Each sample was taken (in glass containers) and mixed, placed on ice, and shipped to the laboratory. Transportation restrictions prevented acid or base preservation.

The following sections describe the sampling method at each sampling point and the sample bottles used. The bottles used are in accordance with the following key:

<u>Code</u>	<u>Container</u>
A	4-liter, linear polyethylene (LPE)
B	40-ml, glass, Teflon lid for Volatile Organics Analysis (VOA)
C	500-ml amber glass, Teflon-lined cap
D	1 gal amber glass, Teflon-lined cap
E	125 ml sterile LPE

3.1 SLUICE/FLUME WATER SAMPLE (BOTTLES B, D, AND E)

The flume water was sampled as potatoes were transferred to the chopper tank. Four 1-liter grab samples were taken, composited and transferred to sample bottles indicated. The water was sampled twice as it came off of the conveyer belt and twice from the agitated catch basin below the conveyer. The water in the flume was to be discharged after the next batch.

3.2 CHOPPER PRODUCT (BOTTLES A, B, AND C)

The chopped potatoes are transferred as a batch to a cooker tank. The valve located at the bottom of the batch tank was used for sampling.

3.3 COOKER PRODUCT (BOTTLES A, B, AND C)

Four 1-liter samples were taken and composited; one at the beginning, two in the middle, and one near the end of the cycle. The liquid portion of the chopper product and washings are also transferred to the cooker tank. Since this stream was not accessible, it was not sampled.

TABLE 3. PROJECT SAMPLES

Description	Sample type	Sampling point	Location ^a
Sluice/flume water	Liquid	Flume basin	15
Chopper product	Slurry	Bottom of batch tank	1
Makeup water	Liquid	Faucet closest to well	2
Cooker product	Slurry	Side valve and fermenter tank influent	3
Fermenter product	Slurry	Side valve on tank	4C/4W
Beer tank	Slurry	Valve before still feed pump (two grabs) and top material within the tank	5,5i 5T
Stillage	Liquid/solid	Thick stillage sampled post SOMAT ^b ; excess and thin stillage sampled at drain pipe	6 7,7G
Interim product	Liquid	Valve at control board (rectifier overhead)	8
Final product	Liquid	Storage tank	9
Cooker washout	Slurry	Drain pipe	11
Fermenter washout	Slurry	Drain pipe	12
Fusel oil	Liquid	Decanter catch	23
Acid bath	Liquid	Batch tank	24
Sparkle bath	Liquid	Batch tank	25

^aCorrelates to Figures 2 and 3^bSolid/Liquid Separator

3.4 MAKEUP WATER (BOTTLES A, B, D, AND E)

The site used an onsite water well. The tap located closest to the well pump (near the chopper tank) was sampled after the water was allowed to run for 10 min.

3.5 FERMENTER PRODUCT (BOTTLES A, B, AND C)

The fermenter product was sampled at the sampling port on the side of the fermenter tank. The sample was composited as the batch was being pumped to the beer tank. Two composite fermenter product samples were taken simultaneously. The first set (4C) was maintained on ice during and after sampling. The second set (4W) was maintained at ambient temperatures for 36 hr in an attempt to approximate the beer tank effluent. The samples are referred to as "cold" and "warm," respectively, in this report. This sampling protocol was necessary due to the inaccessibility of the actual beer tank effluent (beer still feed) stream. Chemical analysis in the laboratory revealed few differences between the "cold" and "warm" fermenter product samples.

3.6 BEER TANK (BOTTLES B AND C)

The beer tank effluent sampling was minimal. Two 500-ml grab samples were taken 16 hr apart. The beer still feed pump had to be turned off to take the sample. This caused operational problems with the stills and was therefore discontinued. An attempt was made to sample through the top of the tank but only the top few inches of material could be penetrated. Therefore, minimal laboratory analysis of the beer tank tops was performed.

3.7 STILLAGE (BOTTLES A, B, C, AND E)

The three stillage (beer still bottoms) streams were sampled. The excess stillage, or stillage overflow, was that material which the solid-liquid separator (SOMAT) could not process and therefore passed through an overflow pipe and into the main waste drain. The overflow was sampled by compositing hourly for 10 hr.

The solid material or thick stillage stream was sampled hourly for 10 hr at the SOMAT outlet. This material normally is loaded onto a truck and subsequently used as cattle feed. Also, one grab sample of the thin stillage stream was taken. This was sampled at the pipe where the SOMAT discharged the liquid to the main waste stream. Flow measurements for the two liquid stillage streams were not taken. However, they both varied considerably (from milliliters to liters per minute) during the sampling period.

3.8 INTERIM PRODUCT (BOTTLE C)

The interim product (rectifier overhead) sample was composited hourly for 10 hr by taking 50-ml grab samples at a test valve located on the outside control panel. The composited sample was sealed and shipped to the laboratory by land carrier.

3.9 FINAL PRODUCT (BOTTLE C)

During the sampling period, the dehydration system malfunctioned and no composite sample could be taken. The final product was, however, sampled from a product storage tank. A 500-ml grab sample was placed in an amber glass bottle and shipped by land carrier to the laboratory.

3.10 COOKER WASHOUT (BOTTLES A, B, C, AND E)

The washout cycle for the cooker tank consists of three rinse-and-dump cycles: before, between, and after the two sterilizing bath cycles. The dump water for the three cycles was composited during one batch cleaning by taking two 400-ml grab samples three times during each dump. The sample was taken at the drain pipe. The three sets were composited, sealed, and placed on ice.

3.11 FERMENTER WASHOUT (BOTTLES B, D, AND E)

The fermenter washout cycle for the fermenter tank is identical to the cooker washout cycle. The sampling and compositing methods were the same as those for the cooker washout sample.

3.12 COMBINED WASHOUT (BOTTLES B AND D)

After delivery to the laboratory, the two wash out cycles were combined. Initially performed analyses were repeated on the combined sample with the exception of the coliform analysis.

3.13 FUSEL OIL (BOTTLE B)

A grab sample of the accumulated fusel oil was taken after the material was mixed for approximately 8 hr. This sample was broken in transit and was replaced with a sample from a later process run; results, therefore, are only generic rather than test specific.

3.14 ACID BATH (BOTTLE C)

A 500-ml grab sample of the agitated acid bath was taken during the sterilization cycle. The sampled batch was to be dumped the following day.

3.15 SPARKLE BATH (BOTTLE C)

A 500-ml grab sample of the agitated sparkle bath was taken during the sterilization cycle. The sampled batch was to be dumped in a few days.

3.16 COMBINED BATH (BOTTLE C)

After delivery to the laboratory, the two bath samples were combined. Subsequently, all initial analytical tests performed on the bath solutions were repeated on the combination sample.

3.17 OTHER SAMPLES

Other samples were taken at various points for possible analysis should the mainstream analyses have shown potential problems. No unexpected results were noted, and additional analyses were not necessary.

SECTION 4

ANALYTICAL TECHNIQUES

The sampling procedures discussed in Section 3 provided samples for detailed analyses in the laboratory. The analytical techniques employed were standard methodologies or optimized methods chosen from available alternatives. This section presents methodologies and references.

The analytical scheme was divided into five tasks:

- Sample bottle preparation
- Sample shipping, log-in, and preservation
- Organics testing
- Inorganic and physical testing
- Quality assurance/quality control (QA/QC)

4.1 SAMPLE BOTTLE PREPARATION

Sampling bottles and equipment were prepared by specific procedures prior to use on this project. Cleaning techniques generally included soap and water wash with deionized water rinsing. Further special cleaning techniques depended on analytical requirements. High-temperature bake-outs on glass, nitric or sulfuric acid washes, and nanograde solvent rinses are a few of these techniques. Trip blanks analyzed with the project assured the cleanliness of sample containers and equipment.

4.2 SHIPPING, LOG-IN, AND PRESERVATION

All project samples discussed in Section 3 were labeled in the field with a sample code number and sample description. Other sampling information was placed in a bound laboratory notebook. The samples were placed in ice chests (with ice) immediately after labeling. Each sample had a volatile organics analysis (VOA) sample bottle prepared in the field and, where appropriate, a sample for bacterial analysis. Samples for extractable organics were placed in amber glass bottles with Teflon-lined lids. Samples were not split out and acid or base preserved in the field due to air transportation restrictions. The samples were maintained on ice and arrived at the laboratory with the sampling team on the evening of December 4, 1981.

The samples of flammable materials (ethanol and fusel oil) had to be shipped by land and no preservation was attempted.

Upon receipt at the laboratory, the samples were logged in. This entailed:

- Issuing and recording laboratory identification numbers
- Recording sample condition and label information
- Issuing sample travelers

A sample traveler identifies specific sample bottles and their required analyses with additional information such as QA/QC requirements.

During the logging in process, samples were split and preserved depending on analytical requirements. This entailed sulfuric acid preservation for total organic carbon (TOC), NO_3^- , phosphorus, nitrogen, chemical oxygen demand (COD), and oil and grease analyses; nitric acid preservation for metals; and sodium hydroxide preservation for cyanide analysis. Regardless of preservation techniques, after the samples were logged in they were stored at 4°C in a walk-in cold room unless analyses were being performed.

4.3 ORGANICS ANALYSES

Methodologies used for organics analyses are based on EPA methods (Reference 3). Samples were analyzed according to procedures listed in Table 4. A brief summary of the methods used is presented in the following paragraphs:

TABLE 4. ANALYTICAL PROCEDURES FOR SAMPLES

Analysis	Method
Volatile organics analysis (purge and trap)	EPA Method 624
Extractable organics by GC/MS	EPA Method 625 (fused silica capillary column)
Pesticides	EPA Method 608
Ethanol/hydrocarbons	GC/MS; GC/FID (flame ionization detector)
Sulfur containing pesticides	GC/Hall Detector, sulfur mode

- Volatile Organics Analysis, VOA (Reference 3, EPA Method 624) -- Volatile organics were determined by the purge and trap technique. Basically, volatile compounds were purged with pure helium and adsorbed on a Tenax trap. The volatile compounds were then desorbed by heating and separated on a 0.2 percent Carbowax 1500 on Carbowax C column.

Quantitation was performed by gas chromatography/mass spectrometry (GC/MS) using a reference standard purged from clean water. Identification of compounds was performed via library search routines using the EPA/NIH library of mass spectra containing 31,000 spectra.

- Base/Neutral/Acid Priority Pollutants, (Reference 3, EPA Method 625) -- Base/neutral and acid priority pollutants were extracted from samples by continuous liquid-liquid extraction.

The sample (1.0 liter for makeup water and 100 ml for the excess stillage sample) was diluted to a volume of 2.0 liters with organics-free water, basified to pH 12, spiked with five surrogate standards (e.g., phenol- d_5 ; 2,4-dinitrophenol- d_4 , nitrobenzene- d_5 ; naphthalene- d_8 and chrysene- d_{12}) at 100 $\mu\text{g/L}$ and extracted overnight with dichloromethane. The sample was then adjusted to a pH of 1.0 and the acids were extracted with fresh solvent for an additional 10 to 12 hr in a liquid-liquid extractor. The extracts were subsequently concentrated to a volume of 1-ml.

Analysis of samples was performed by GC/MS using a 30m by 0.32 mm ID fused silica capillary column coated with SE-54. The temperature program used for the combined base/neutral and acidic extracts allowed gas chromatographic separation of all the base/neutral/acid priority pollutants. Immediately prior to GC/MS analysis each sample extract was spiked with four internal standards (e.g., decane- d_{22} , 1-fluoronaphthalene; anthracene- d_{10} ; terphenyl- d_{12}) at 20 ng/ μL . The internal standards were added to measure the performance of the mass spectrometer over the entire mass range of compounds being determined and to correct for possible discrimination of the splitless injection during sample transfer onto the capillary column.

- Pesticides (Reference 3, EPA Method 608) -- Samples of makeup water and stillage were extracted for pesticides with dichloromethane at neutral pH. Analyses were performed by gas chromatography with electron capture detection according to EPA Method 608.
- Ethanol and Other Organics -- The interim and final products were quantitatively analyzed for ethanol content by two methods. An ethanol hydrometer with temperature calibration was used. Secondly, a gas chromatographic method was used for samples of the two products and various process streams. Ethanol was separated on a 5 percent Carbowax 20M on Carbowax B/AW, 80-120 mesh columns.

Other organic compounds, such as other alcohols and aldehydes, were screened for by GC/MS using an 0.2 percent Carbowax 1500 on Carbopack C column. No other organics were detected in the sample at a detection limit of approximately 50 ppm, interpreted within the restrictions of the methodology.

- Ethanol and Other Organics -- The fusel oil sidecut, which is essentially dumped as convenient, was diluted 1:1000 with methanol and analyzed by gas chromatography/mass spectrometry. The major species were identified by manual and computerized library comparison of the mass spectra. Quantification of the composition was accomplished by integration of the peaks in the total ion current chromatogram.
- Special Sulfur-Containing Pesticides (metribuzin and disulfoton) -- Analysis of metribuzin and disulfoton was performed by gas chromatography with electrolytic conductivity detection (Hall detector in sulfur mode). The following conditions were used:

Hall Detector, Sulfur Mode

Attenuation: 100 x 8
Solvent flow: 5 (setting)
Solvent: Methanol
Reactor Temperature: 850°C
Vent time: 0.5 min
Air flow: 50 ml/min
Column: 10 percent DEGS on Suppelcoport 100/120 mesh
Temperature program: 175°C to 200°C at 8°C/min; final held 15 min

Thiabendazole and chloroprofan are not amenable to gas chromatography, and therefore could not be detected in the samples.

4.4 INORGANIC CHEMICAL AND PHYSICAL CHARACTERISTIC TESTING

Analytical methodologies used for the general chemical analyses were based on "Standard Methods for the Examination of Water and Wastewater," 14th Edition APHA, AWWA, WPCF (Reference 4) and "Methods for the Analysis of Water and Wastes", EPA, March 1979 (Reference 5). Aqueous samples were analyzed according to Table 5. The analytical procedures for high-solids samples were basically the same as for the liquid samples except that analyses of these slurries generally entailed more sample preparation and more rigorous digestion.

The following is a summary of the test methods employed on the project samples. Following each method is a reference and brief description of the method.

TABLE 5. GENERAL CHEMICAL ANALYSIS

Parameter	Method
BOD ₅	5-day incubation, sample analyzed for oxygen depletion
COD	Acid dichromate reflux, back titrate with ferrous ammonium sulfate
TOC	Conversion to CO ₂ , infrared quantitation
Total suspended solids	Gravimetric, 105°C, weigh residue on filters
Total solids	Gravimetric, 105°C, weight of residue
Phenolics (total recoverable)	Distill, aminoantipyrine color, CHCl ₃ extraction
Cyanides (total)	Distill, barbituric acid colorimetry
Ammonia	Distill, followed by nesslerization
Nitrate	Brucine colorimetric
Sulfate	Turbidimetric
Phosphorus (total)	Nitric/sulfuric acid digest, ascorbic acid colorimetry
Specific conductance	Wheatstone bridge conductivity
Metals ^a	Atomic absorption spectrophotometry following acid digestion. Analysis by cold-vapor flameless AA (Hg), flame and graphite furnace analyses as appropriate for others
pH	Electrometric
Total Kjeldahl nitrogen	Sulfuric acid mercuric oxide digestion, distillation, nesslerization
Oil and grease	Partition/gravimetric, freon extraction
Total and fecal coliform	Multiple tube fermentation (gas producers)
Sugars, reducing	Condense with orthotoluidine in acetic acid followed by spectrophotometry on liquid portion of samples

^aMetals: Al, Sb, As, Ba, Be, Bi, Ca, Cd, Cr, Cu, Fe, Pb, Mg, Mn, Hg, Ni, Se, Ag, Tl, Ti, and Zn

- Biochemical Oxygen Demand, BOD_{5day} (Reference 4, Method 507) -- Portions of samples were incubated in the dark at 20°C for 5 days. Oxygen depletion was measured using an oxygen probe.
- Chemical Oxygen Demand, COD (Reference 4, Method 508) -- Samples were digested under reflux in a mixture of sulfuric acid and potassium dichromate. Dichromate consumption was measured.
- Total Organic Carbon, TOC (Reference 5, Method 415.1) -- Samples were analyzed on a Beckman 915 TOC Analyzer by Brown and Caldwell, Environmental Sciences Division. Organic carbon was converted to carbon dioxide and quantified using an infrared detector.
- pH Value (Reference 4, Method 424) -- Samples were analyzed for pH using an Altex Model 3560 digital pH meter. Solid samples were extracted with deionized water and the solution pH determined.
- Specific Conductance (Reference 4, Method 205) -- Sample conductivities were measured using a Lab-line Lectro Mho meter. The instrument measured the electrical conductivity of the sample.
- Total Suspended Solids, TSS (Reference 4, Method 208D) -- Samples were filtered and the residue on the filter was dried at 103° to 105°C. The gain in filter weight for a given volume filtered was the total suspended solids.
- Total Solids, TS (Reference 4, Method 208A) -- Portions of the samples were dried at 103° to 105°C. The residue was determined gravimetrically.
- Phenolics (Reference 4, Method 510A, 510B) -- Samples were distilled. The phenol in the distillate were reacted with 4-aminoantipyrine in the presence of potassium ferricyanide to form a colored antipyrine dye. The dye was extracted with chloroform. The concentration of extracted dye was determined spectrophotometrically.
- Cyanide (Reference 4, Method 413A, B, D) -- The cyanide content of the samples was determined following the preliminary distillation of HCN from an acidified sample. The HCN was absorbed in a NaOH solution. The NaOH solution was analyzed for cyanide using the pyridine barbituric acid colorimetric method.
- Ammonia Nitrogen (Reference 4, Method 418A, B) -- Samples were distilled from buffered basic solution into boric acid absorbant. The distillates were analyzed for ammonia content using the nesslerization (colorimetric) method.
- Total Kjeldahl Nitrogen (Reference 4, Method 421) -- Samples were digested with a mixture of sulfuric acid, mercuric oxide and potassium sulfate. This releases most organic (nitrogens). The

ammonia this produced was then distilled from the solution and absorbed in boric acid. The distillates were analyzed using the nesslerization method.

- Nitrate Nitrogen (Reference 4, Method 419D) -- Nitrates were determined using the Brucine colorimetric method. Solid or high suspended solid samples were extracted with dilute sulfuric acid and filtered preceding analysis.
- Sulfate (Reference 4, Method 427C) -- Sulfates were determined turbidimetrically. Solid or high suspended solid samples were extracted with dilute hydrochloric acid and filtered preceding analysis. Sulfate content was determined by mixing portions of the extract with conditioning reagent. Barium chloride crystals were added and the barium sulfate crystals formed were quantified using a nephelometer.
- Phosphorus, Total (Reference 4, Method 425C, F) -- Samples were digested in nitric and sulfuric acids to release organically bound phosphorus. Following digestion, phosphorus was determined using ascorbic acid colorimetry.
- Metals, Total (see Table 6) -- Metals were determined by atomic absorption spectrophotometry. Samples were digested with nitric acid. Mercury was determined by the cold vapor technique following permanganate-persulfate digestion. Other metals were determined by either flame or graphite furnace atomization of the nitric acid digest. A Perkin-Elmer Model 460 atomic absorption spectrophotometer equipped with an HGA Model 2100 controller, ramp accessory, and auto sampling system was used.

Table 6 lists the method reference for each of the metals. Deviations from the standard procedures were adaptations to the nature of the samples submitted. Deviations were primarily in quantities and final concentrations of acid in the prepared samples.

- Oil and Grease (Reference 4, Model 502A, C, and D) -- The aqueous sample was acidified to pH <2 and extracted with Freon 112. The Freon was evaporated and the residue weighed.

The effluent sample was acidified and filtered through a 0.45 μ filter. The filtrate was analyzed by the above extraction procedure. The residue on the filter was dried with MgSO₄·H₂O and the filter and suspended solids soxhlet extracted overnight with Freon 112. The resulting extract was evaporated at 70°C in a tared vessel. The vessel was dessicated to constant weight. Losses of volatile compounds cannot be prevented using this procedure.

- Total and Fecal Coliform (Reference 4, Method 908) -- Serial dilutions of samples are inoculated into lactose broth

TABLE 6. ANALYSIS METHOD FOR METALS DETERMINATION

Metal	Reference	Method
Aluminum	5	201.1
Antimony	5	204.2
Arsenic	5	206.2
Barium	5	208.1, 208.2
Beryllium	5	210.1, 210.2
Bismuth	6	Flame/furnace
Cadmium	5	213.1, 213.2
Calcium	5	215.1
Chromium	5	218.1, 218.2
Copper	5	220.1, 220.2
Iron	5	236.1
Lead	5	239.1, 239.2
Magnesium	5	242.1
Manganese	5	243.1, 243.2
Mercury	5	245.1
Nickel	5	249.1
Selenium	5	270.2
Silver	5	272.1, 272.2
Thallium	5	279.2
Titanium	5	283.1, 283.2
Zinc	5	289.1

(presumptive) and incubated. Positive tubes, detected by gas formation, are subjected to confirmation in brilliant green lactose bile broth and to the fecal coliform procedure. The fecal coliform procedure employs inoculation into EC media. Quantification is by number of positive tubes and is a statistical measurement of the most probable number of viable organisms per 100 ml of sample.

- Total Reducing Sugars (Reference 7) -- The samples were centrifuged and the supernatant analyzed as follows. The reducing sugars (e.g., glucose, galactose) condense with ortho-toluidine in glacial acetic acid during heating to produce a blue-green color which is measured spectrophotometrically at 595 nm. Glucose was used as the standard and results are reported as values relative to equivalent amounts of glucose.

4.5 QA/QC

Approximately 40 percent of the analytical effort was involved with QA/QC activities. The project specific QA/QC program had the objective to meet or exceed client requirements for precise results. Some features of the QA/QC procedures are summarized in the following paragraphs.

Upon completion of the sampling trip, the project chemist reviewed the analytical requirements with the sample custodian during the logging in process. The chemists and analysts discussed with the laboratory supervisors alternative procedures before the analyses commenced. Thus, the samples requiring analysis and procedures to be followed were clearly specified at the outset of the analytical program.

The laboratory analysis portion of the QA/QC program entailed several phases from glassware preparation to the reporting of results, most of these clearly specified in formalized procedures. Any alteration of procedures was reviewed with the project chemist before testing began.

The analytical QA/QC procedures entailed blank, duplicate, spike, method standard, and reference sample analyses. Calibration standards were of primary standard grade, NBS traceable, or certified purity. Specific results for the duplicate, spike, and EPA supplied performance analyses are included in Appendix A.

To assure the integrity of the reported results, the project chemist reviewed data with the analysts and discussed the results. Reported values were transcribed directly from the laboratory book to the handwritten laboratory draft. The typed draft for review was then checked against the original laboratory draft.

By using these specific procedures and several other integral parts of the laboratory QA/QC program, the quality of the analytical work was documented and assured.

SECTION 5

ANALYTICAL RESULTS AND DISCUSSION

The analytical procedures specified in Section 4 were used to generate the data presented in this section. Also included are discussions of results, conclusions, and recommendations.

5.1 LABORATORY ANALYTICAL RESULTS

The laboratory analytical sample matrix is shown in Table 7. Analytical results for the ethanol plant are presented in Tables 8 through 14. The tables are presented in the following order:

- Ethanol content, sugar content
- Conventional parameters
- Metals
- Cyanide, phenolics, nutrients, and oil and grease
- Priority pollutant organics
- Selected pesticides

5.2 DISCUSSION OF ANALYTICAL METHODS

Certain qualifications and limitations of the analytical methodologies are presented in this section.

5.2.1 Ethanol, Sugar, and Other Nonpriority Pollutant Organics

The true values for ethanol and sugar content of the fermenter and beer tank samples may be different from those reported. These samples are biochemically active, and chemical changes during the sampling to analysis time interval are quite possible even though the samples were refrigerated. These samples were also screened for other organic compounds by the GC/MS procedure outlined in Section 4. Within the limitations of the procedure no other organic compounds were detectable at levels greater than approximately 50 ppm.

The fusel oil sidecut was also analyzed for organics, specifically ethanol and higher alcohols as discussed in Section 4. Although the sample

TABLE 7. ANALYTICAL SAMPLE MATRIX

Parameter																						
ID No.	Stream	BOD ₅	COD	TOC	TSS	TS	pH	Conductivity	21 metals ^a	P. P. organics ^b	Oil and grease	Coliform	Phenolics	Cyanide	SO ₄ -2	NO ₃ -1	P, total	NH ₃ , TONC, TKN	EtOH, R-H's	Sugar	Four pesticides	Densit ^d
-1	Chopper product	x	x	x		x	x														x	x
-2	Makeup water	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x	x
-3	Cooker product	x	x	x	x	x	x														x	x
-4C	Fermenter product (cold)	x	x	x	x	x	x														x	x
-4W	Fermenter product (warm)	x	x	x	x	x	x														x	x
-5I	1st Beer tank effluent	x					x	x												x ^e		x
-5	2nd beer tank effluent	x				x	x	x												x ^e		x
-5T	Beer tank tops						x	x														
-6	Excess stillage	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x
-7	Thick stillage	x	x	x			x	x														
-7G	Thin stillage	x	x	x	x	x	x	x														x
-8	Distillation product																			x		
-9	200-proof dehydration product																			x		
-11	Washout cooker	x					x	x				x										x
-12	Washout fermenter	x					x	x				x										x
-13	Washout combination	x	x	x	x	x	x	x														x
-15	Sluice water	x	x			x	x	x	x			x										x
-23	Fusel oil																			x		
-24	Acid bath	x					x	x														
-25	Sparkle bath	x					x	x														
-27	Bath combination	x	x	x	x	x	x	x														
-30	Field/lab blank	x	x	x	x	x			x	x	x	x	x	x	x	x	x	x	x	x	x	x

^a21 metals are for "total" analyses and are: Al, Sb, As, Ba, Be, Bi, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Hg, Ni, Se, Ag, Tl, Ti, and Zn

^bAcid extractables, base/neutral extractables, and VOA -- by fused silica capillary column, Pesticides (organochlorine) -- GC/EC

^cTON, Total organic nitrogen derived from TKN less NH₃

^dDensities have been determined but are not reported. They are used for conversions from weight/weight units to weight/volume units (i.e. mg/kg to mg/L)

^eEthanol only

x = Being measured

TABLE 8. ETHANOL AND SUGAR CONTENT

ID No.	Stream	Ethanol by GC ^a (volume percent)	Sugar ^b (wt/volume percent)
-3	Cooker product	NA	15
-4C	Fermenter product (cold)	9.1	0.11
-4W	Fermenter product (warm)	8.8	0.04
-5i	Beer tank (1st grab)	4.8	NA
-5	Beer tank (2nd grab)	5.0	NA
-6	Excess stillage	0.45	0.03
-8	Interim product	96 (97)	NA
-9	Final product	100 ^c (99.5)	NA

^aResults in parentheses are hydrometer results

^bReducing sugars, as glucose

^cActual measurement was 102 percent due to experimental variance

NA -- Not applicable

TABLE 9. FUSEL OIL ALCOHOL COMPOSITION

Compound	Composition normalized to 100 percent
Ethanol	72
2-propanol	4
Pentanol (isomer)	2
Pentanol (isomer)	<u>22</u>
	100

TABLE 10. VALUES FOR CONVENTIONAL PARAMETERS (mg/L, UNLESS NOTED OTHERWISE)

ID No.	Stream	Parameter								
		BOD ₅ ^a	COD	TOC	TSS (103° to 105°C)	TSS (103° to 105°C)	pH ^c electrometric @ 25°C	Specific conductivity umhos/cm @ 25°C	Total Coliform ^f	Fecal Coliform ^f
-1	Chopper product	47,000	160,000	33,000	-	16% wt	5.50	--	--	--
-2	Makeup water	<2	<5	3.3	<5	308	7.39	442	9.1	<2
-3	Cooker product	107,000	209,000	57,500	18,000	18% wt	4.97	--	--	--
-4C	Fermenter product (cold)	102,000	216,000	36,000	35,000	6.3% wt	4.88	--	--	--
-4W	Fermenter product (warm)	102,000	201,000	34,000	32,000	6.1% wt	4.88	--	--	--
-5i	1st beer tank effluent	59,000	--	--	--	5.8% wt	4.58	--	--	--
-5	2nd beer tank effluent	54,000	--	--	24,800	6.2% wt	4.78	--	--	--
-5T	Beer tank tops	--	--	--	--	10.7% wt	5.16	--	--	--
-6	Excess stillage	20,000	59,800	22,000	22,000	5.5% wt	4.74	13,600	<20	<20
-7	Thick stillage	25,000 ^g	74,700 ^g	29,000 ^g	--	8.1% wt	4.65	--	--	--
-7G	Thin stillage	18,000	54,800	21,000	24,700	54,000	4.67	14,900	--	--
-11	Washout cooker	17,100	--	--	--	29,100	5.51	--	≥24,000	9,200
-12	Washout fermenter	4,200	--	--	--	4,700	2.76	--	460	20
-13	Washout combination	9,900	22,000	7,700	3,080	10,100	4.45 ^d	1,950	--	--
-15	Sluice water	1,980	7,500	--	11,200	12,200	6.90	1,130	≥24,000	270
-24	Acid bath	780	--	--	--	1,750	6.64 4.99 ^e	--	--	--
-25	Sparkle bath	2,700	--	--	--	5,600	6.14 4.46 ^e	--	--	--
-27	Bath combination	2,200	4,600	1,600	880	3,100	5.43 ^d 4.63 ^e	1,020	--	--
-30	Field/lab blank	<2	<5	1.9	NA	<10	--	<1	<2	<2

^aMost of the BOD determinations were performed a second time to bring results in a qualifiable range.^bTotal solids method was 24 hr at 103°-105°C^cFirst pH determinations were performed on 12/5/81^dCombinations were measured on 12/9/81^eRechecks were measured on 2/22/81^fUnits are MPN/100ml (most probable no. per 100ml)^gmg/kg

TABLE 11. VALUES FOR METALS ($\mu\text{g/L}$)^a

Parameter \	Steam	I.D. No. 2 Makeup water	I.D. No. 6 Excess stillage
Aluminum, Al		<30	22,300
Antimony, Sb		<10	<20
Arsenic, As		<10	<20
Barium, Ba		50	430
Beryllium, Be		<1	1.7
Bismuth, Bi		<20	<200
Cadmium, Cd		<0.5	8.5
Calcium, Ca		67,000	140,000
Chromium, Cr		<5	125
Copper, Cu		8	1,500
Iron, Fe		<30	29,500
Lead, Pb		<5	16
Magnesium, Mg		16,000	176,000
Manganese, Mn		<20	1,500
Mercury, Hg		<0.5	7
Nickel, Ni		<10	<70
Selenium, Se		<10	<20
Silver, Ag		<0.6	1.5
Thallium, Tl		<5	<10
Titanium, Ti		<100	1,300
Zinc, Zn		180	2,900

^aField/lab blanks showed no significant contamination

TABLE 12. VALUES FOR CYANIDE, PHENOLICS, NUTRIENTS, AND OIL AND GREASE
(mg/L UNLESS OTHERWISE NOTED)^a

Stream Parameter	ID No. 2 Makeup water	ID No. 6 Excess stillage
Oil and grease ^b (Freon extractables)	<5	167
Total phenols as C ₆ H ₅ -OH	<0.01	0.23
Total cyanide as CN-	<0.01	0.04
Sulfate	49	2,400
Nitrate as N	1.2	2.7 mg/kg
Ammonia as N	<0.05	270
Organic nitrogen as N	0.33	1,840
Total Kjeldahl nitrogen as N	0.33	2,110
Total phosphorus as P	0.01	340

^aField/lab blanks showed no significant contamination

^bSee the discussion on page A-1

TABLE 13. ORGANIC PRIORITY POLLUTANT VALUES

Stream	I.D. No. 2 Makeup water ($<1 \mu\text{g/L}$) ^a	I.D. No. 6 Excess stillage ($<10 \mu\text{g/L}$) ^a
Parameter		
<u>Volatiles</u>		
2V Acrolein	ND	ND
3V Acrylonitrile	ND	ND
4V Benzene	ND	ND
6V Carbon tetrachloride	ND	ND
7V Chlorobenzene	ND	ND
10V 1,2-dichloroethane	ND	ND
11V 1,1,1-trichloroethane	ND	ND
13V 1,1-dichloroethane	ND	ND
14V 1,1,2-trichloroethane	ND	ND
15V 1,1,2,2-tetrachloroethane	ND	ND
16V Chloroethane	ND	ND
19V 2-chloroethylvinyl ether	ND	ND
23V Chloroform	ND	ND
29V 1,1-dichloroethylene	ND	ND
30V 1,2-trans-dichloroethylene	ND	ND
32V 1,2-dichloropropane	ND	ND
33V 1,3-dichloropropylene	ND	ND
38V Ethylbenzene	ND	ND
44V Methylene chloride	ND	ND
45V Methyl chloride	ND	ND
46V Methyl bromide	ND	ND
47V Bromoform	ND	ND
48V Dichlorobromomethane	ND	ND
49V Trichlorofluoromethane	ND	ND
50V Dichlorodifluoromethane	ND	ND
51V Chlorodibromomethane	ND	ND
85V Tetrachloroethylene	ND	ND
86V Toluene	ND	ND
87V Trichloroethylene	ND	ND
88V Vinyl chloride	ND	ND
<u>Pesticides</u>		
89P Aldrin	ND	ND
90P Dieldrin	ND	ND
91P Chlordane	ND	ND

(continued)

^aDetection limit
 ND -- Not detectable

TABLE 13. Continued

Stream Parameter	I.D. No. 2 Makeup water ($<1 \mu\text{g/L}$)	I.D. No. 6 Excess stillage ($<10 \mu\text{g/L}$)
<u>Pesticides (continued)</u>		
92P 4,4'-DDT	ND	ND
93P 4,4'-DDE	ND	ND
94P 4,4'-DDD	ND	ND
95P α -endosulfan	ND	ND
96P β -endosulfan	ND	ND
97P Endosulfan sulfate	ND	ND
98P Endrin	ND	ND
99P Endrin aldehyde	ND	ND
100P Heptachlor	ND	ND
101P Heptachlor epoxide	ND	ND
102P α -BHC	ND	ND
103P β -BHC	ND	ND
104P δ -BHC	ND	ND
105P γ -BHC	ND	ND
106P PCB-1242	ND	ND
107P PCB-1254	ND	ND
108P PCB-1221	ND	ND
109P PCB-1232	ND	ND
110P PCB-1248	ND	ND
111P PCB-1260	ND	ND
112P PCB-1016	ND	ND
113P Toxaphene	ND	ND
<u>Acid Compound</u>		
21A 2,4,6-trichlorophenol	ND	ND
22A Chloro-m-cresol	ND	ND
24A 2-chlorophenol	ND	ND
31A 2,4-dichlorophenol	ND	ND
34A 2,4-dimethylphenol	ND	ND
57A 2-nitrophenol	ND	ND
58A 4-nitrophenol	ND	ND
59A 2,4-dinitrophenol	ND	ND
60A 4,6-dinitro-o-cresol	ND	ND
64A Pentachlorophenol	ND	ND
65A Phenol	ND	ND

(continued)

ND -- Not detectable

TABLE 13. Continued

Stream		I.D. No. 2	I.D. No. 6
Parameter		Makeup water ($<1 \mu\text{g/L}$)	Excess stillage ($<10 \mu\text{g/L}$)
<u>Base/Neutral Compounds</u>			
1B	Acenaphthene	ND	ND
5B	Benzidine	ND	ND
8B	1,2,4-trichlorobenzene	ND	ND
9B	Hexachlorobenzene	ND	ND
12B	Hexachloroethane	ND	ND
18B	Bis(2-chloroethyl)ether	ND	ND
20B	2-chloronaphthalene	ND	ND
25B	1,2-dichlorobenzene	ND	ND
26B	1,3-dichlorobenzene	ND	ND
27B	1,4-dichlorobenzene	ND	ND
28B	3,3'-dichlorobenzidine	ND	ND
35B	2,4-dinitrotoluene	ND	ND
36B	2,6-dinitrotoluene	ND	ND
37B	1,2-diphenylhydrazine (as azobenzene)	ND	ND
39B	Fluoranthene	ND	ND
40B	4-chlorophenyl phenyl ether	ND	ND
41B	4-bromophenyl phenyl ether	ND	ND
42B	Bis(2-chloroisopropyl)ether	ND	ND
43B	Bis(2-chloroethoxy)methane	ND	ND
52B	Hexachlorobutadiene	ND	ND
53B	Hexachlorocyclopentadiene	ND	ND
54B	Isophorone	ND	ND
55B	Naphthalene	ND	ND
56B	Nitrobenzene	ND	ND
61B	N-nitrosodimethylamine	ND	ND
62B	N-nitrosodiphenylamine	ND	ND
63B	N-nitrosodi-n-propylamine	ND	ND
66B	Bis(2-ethylhexyl)phthalate	ND	ND
67B	Butylbenzyl phthalate	ND	ND
68B	Di-n-butyl phthalate	ND	ND
69B	Di-n-octyl phthalate	ND	ND
70B	Diethyl phthalate	ND	ND
71B	Dimethyl phthalate	ND	ND
72B	Benzo(a)anthracene	ND	ND
73B	Benzo(a)pyrene	ND	ND
74B	3,4-benzofluoranthene	ND	ND

(continued)

ND -- Not detectable

TABLE 13. Concluded

Stream		I.D. No. 2	I.D. No. 6
Parameter		Makeup water ($<1 \mu\text{g/L}$)	Excess stillage ($<10 \mu\text{g/L}$)
<u>Base/Neutral Compounds (concluded)</u>			
75B	Benzo(k)fluoranthene	ND	ND
76B	Chrysene	ND	ND
77B	Acenaphthylene	ND	ND
78B	Anthracene	ND	ND
79B	Benzo(ghi)perylene	ND	ND
80B	Fluorene	ND	ND
81B	Phenanthrene	ND	ND
82B	Dibenzo(a,h)anthracene	ND	ND
83B	Indeno(1,2,3-cd)pyrene	ND	ND
84B	Pyrene	ND	ND

(concluded)

ND -- Not detectable

TABLE 14. SELECTED PESTICIDES ($\mu\text{g/L}$)

Compound	Stream	
	ID No. 1 chopper product	ID No. 15 sluice water
Metribuzin	<10	<2
Disulfoton	<10	<2
Unknown	-- ^a	12
Chloroprophan	NC	NC
Thiabendazole	NC	NC

^aUnidentified chromatographable sulfur compound which eluted between disulfoton and metribuzin

Note

NC -- Not amenable to gas chromatography

obtained during the test period was broken in transport, a substitute sample was obtained from a subsequent batch. The results presented are, therefore, only representative of this stream composition.

5.2.2 Conventional Parameters

The BOD and pH analyses were first performed within 48 hr of sampling. Several BOD measurements were out of the quantifiable range; the samples were rerun when this became apparent. The results reported should be interpreted with this delay in mind.

The initial pH measurements were delayed on the combined samples until 1 week after sampling. The pH measurements on the combined samples seemed inconsistent with the initial bath and washout sample pH measurements. It would appear from the data that the pH values were dropping over time. Possibly this occurred due to oxidation of ethanol to acetic acid and/or carbon dioxide formation from biological activity.

5.2.3 Nutrients and Oil and Grease

Oil and grease results for the excess stillage sample are probably low. Analysis of reference materials demonstrated a significant loss of volatile compounds using the prescribed drying at 70°C with a final nitrogen purge. In the future, evaporation of Freon at ambient temperatures would appear more reliable. Alternatively, the partition-infrared method would minimize losses of volatile compounds as no evaporation of the Freon is required.

5.2.4 Priority Pollutant, Pesticides, and Organics

Analytically, no matrix problems with the analysis of the project samples were encountered. Blank and sample spikes produced acceptable results. The only limitation deals with the volatile organics analysis. The VOA analyses were not performed until 6 weeks after sampling. The data for the VOA analysis is of low reliability due to the long holding time and high biochemical activity of samples. However, as the stillage has been heated and purged to a degree in the beer still, the presence of volatile priority pollutants was not expected.

5.2.5 Selected Pesticides

Four pesticides* were identified as possible contaminants based on information supplied by the Idaho Department of Agriculture, the feed material supplier, and plant personnel. Minimal use of biocides is allowed because higher levels can cause interference with the processes, particularly during fermentation. The four pesticides were the only ones in use or previously in use by the plant and feed supplier. Only metribuzin and disulfoton were analyzed for since chloroprophan and thiabendazole are not amenable to gas chromatography. A high-pressure liquid chromatograph (HPLC)

*Metribuzin, disulfoton, chloroprophan, and thiabendazole.

method as an alternative method is proposed since the GC methods probably decompose the compounds during heating.

5.3 DISCUSSION OF ANALYTICAL RESULTS

The plant waste streams showed characteristics that could impact the water quality of the receiving stream. The most significant was oxygen demand (for all process and waste streams). This is apparent from the BOD, COD, and TOC results.

Although the discharges from this plant were contained, direct discharge of these streams to waterways could severely affect the waters by depleting available oxygen. Discharge of these materials would most severely affect oxygen-sensitive areas such as surface waters.

The excess stillage stream exhibited high nutrient content; thus, these waste waters could be expected to stimulate rapid plant growth.

The pH throughout the system (liquid and solid streams) was in the range of 4.4 to 6.0 to facilitate the action of the enzymes and yeast in the fermentation process. The effects of these wastes would depend on the relation of their acidity to the buffering capacity of the receiving environment. A pH drop of any magnitude could result in aquatic population shifts and possible destruction, corrosion of metallic systems, and agricultural crop damage. With regard to crop damage, acidity of irrigation waters are usually of little consequence over a pH range of 4.5 to 9.0 since the soil is also a buffered system. It should be noted that the pH of the washout streams occurring from the alcohol production were at the very low end of this range and could be toxic to plants.

The results of the metals analyses indicate that the wastes have significant levels of several metals. Without further testing, the source of these metals cannot be definitively isolated; however, most can be attributed to the materials added (e.g., epsom salt) and the leaching of metals from the process equipment (primarily stainless steel and aluminum).

No priority pollutant organics were detected in the samples. One unknown sulfur compound was detected at 12 $\mu\text{g/L}$ in the flume water. With the exception of alcohols, no compounds of significance were detected in the samples. Analysis of the fusel oil indicated that only alcohols were present with ethanol still comprising the largest fraction. Only a few gallons of fusel oil are produced daily and transferred to a landfill disposal site.

Bacteriological quality is a concern for the flume water and washout waters. Coliform analyses are performed as indicator tests for possible health-related organisms such as fecal streptococcus. More testing would be required to preclude bacterial sources other than the feedstock itself.

5.4 CONCLUSIONS AND RECOMMENDATIONS

The preliminary results of this sampling and analysis are consistent with those from other fuel alcohol plants using a variety of other feedstocks. Thus, the problems to be addressed and methods of addressing them may be similar.

The effluents from this plant contain significant water quality variables and pollutants that could degrade receiving waters:

- Oxygen demand (TOC, COD, BOD)
- Solids (TSS, TS, specific conductance)
- Nutrients (nitrogen and phosphorus)
- Metals (Al, Cd, Ca, Cr, Cu, Fe, Mg, Mn, Hg, Ti, and Zn)
- Bacteria (total and fecal Coliform)
- Corrosivity, low pH

Although primary concern for environmental impacts should be with those normal discharges from the process, one must also be concerned with the "dumping" of poor batches and the disposal of the solid materials other than by use as a byproduct (i.e., as an animal feedstock). The overall results indicate wastestreams of sufficient concentration to warrant concern regarding the environmental impacts of effluents from the ethanol plant. However, the environmental problems caused by nonuse of culled potatoes must also be considered.

The low pH of the liquid streams potentially has two effects:

- Adverse effect on crops if used in land farming
- Corrosion of process equipment

It would appear that these streams should be neutralized to a pH of 6.0 to 8.0 as early as possible. Since the acidic level is required for the fermentation process, a realistic point for neutralization would be downstream of the fermentation tanks in the beer tank. The chemical (a buffer salt) used for neutralization at this point must be benign with respect to the byproduct use.

REFERENCES

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4. "Standard Methods for the Examination of Water and Wastewater," 14th Edition, 1975. APHA, AWWA, WPCF, Washington, D.C.
5. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1979.
6. "Standard Operating Conditions Manual," Perkin-Elmer Corporation, Norwalk, Connecticut, September 1976.
7. Dow Diagnostics Glucose Determination Kit. Available from Dow Chemical Company, P. O. Box 68511, Indianapolis, Indiana 46268.

APPENDIX A

QUALITY ASSURANCE/QUALITY CONTROL RESULTS

This section presents, in tabular format, the results for the replicate, spiked, and performance check samples analyses. Performance samples were analyzed for the priority pollutant organics, but are not evaluated in this report.

During trials on the performance evaluation samples, results for the nitrate analysis and oil and grease analysis were not within acceptance limits. Modifications of both procedures were made and subsequently reference samples of known value analyzed. The results are presented herein. The problem with the oil and grease analysis was caused by drying the Freon extracts at the prescribed 70°C. Evaporation of Freon at ambient temperatures produces results within acceptance limits. The problem with the nitrate (by brucine) analysis was in drawing of the calibration curve. Modification of the laboratory nitrate by brucine standard operating procedure has been performed.

Only one set of replicate or spiked sample results is given for each parameter. Several parameters (solids, BOD, COD, phenols, CN, NO₃, NH₃/TKN, P, and selected metals) had replicate analysis performed on all samples and others had additional spikes. Given the matrices encountered this was necessary to generate reliable data. When compounds were at or below detection limits generally only one matrix spike was necessary.

TABLE A-1. REPLICATE ANALYSES

Parameter	Sample	Units	X ₁	X ₂	$\bar{X}$	2S	2S as rel %
Ethanol	Fermenter (cold)	% by vol	9.23	9.05	9.14	0.25	2.8
Sugars, as glucose	Fermenter (cold)	% w/v	0.11	0.12	0.115	0.014	12
BOD	Fermenter (cold)	mg/L	99,000	105,000	102,000	8,500	8.3
COD	Cooker product	mg/L	217,000	201,000	209,000	23,000	11
TOC	Cooker product	mg/L	58,000	57,000	57,500	1,400	2.5
TSS (suspended solids)	Excess stillage	mg/L	20,000	23,000	21,500	4,200	20
TS (total solids)	Excess stillage	% by wt	5.5	5.5	5.5	0	0
pH	Sluice/flume	pH	6.90	6.90	6.90	0	0
Specific conductance	Makeup water	umhos/cm	442	452	447	14	3.2
Oil and grease	Excess stillage	mg/L	165	168	167	4.2	2.5
Phenols, total as C ₆ H ₅ OH	Excess stillage	ug/L	240	210	225	42	19
Cyanide	Excess stillage	ug/L	40	40	40	0	0
Sulfate	Excess stillage	mg/L	2,430	2,380	2,405	71	2.9
Nitrate, as N	Excess stillage	mg/kg	2.9	2.5	2.7	0.57	21
Ammonia, as N	Excess stillage	mg/L	250	290	270	57	21
Organic nitrogen	Excess stillage	mg/L	1,810	1,870	1,840	85	4.6
Kjeldahl nitrogen	Excess stillage	mg/L	2,080	2,140	2,110	85	4.0
Phosphorus, total	Excess stillage	mg/L	In quadruplicate		338	42	12
Aluminum, Al	Excess stillage	ug/L	21,400	23,200	22,300	2,500	11
Antimony, Sb	Excess stillage	ug/L	<20	<20	<20	0	0
Arsenic, As	Excess stillage	ug/L	<20	<20	<20	0	0
Barium, Ba	Excess stillage	ug/L	430	430	430	0	0
Beryllium, Be	Excess stillage	ug/L	1.5	1.8	1.65	0.42	26
Bismuth, Bi	Excess stillage	ug/L	<200	<200	<200	0	0
Cadmium, Cd	Excess stillage	ug/L	8.8	8.2	8.5	0.85	10
Calcium, Ca	Excess stillage	ug/L	130,000	150,000	140,000	28,000	20
Chromium, Cr	Excess stillage	ug/L	130	120	125	14	11
Copper, Cu	Excess stillage	ug/L	1,450	1,550	1,500	140	9.4
Iron, Fe	Excess stillage	ug/L	28,700	30,300	29,500	2,300	7.7
Lead, Pb (Det Lim.=10)	Excess stillage	ug/L	12	20	16	11	69
Magnesium, Mg	Excess stillage	ug/L	175,000	177,000	176,000	2,800	1.6
Manganese, Mn	Excess stillage	ug/L	1,600	1,400	1,500	280	19
Mercury, Hg	Excess stillage	ug/L	7	7	7	0	0
Nickel, Ni	Excess stillage	ug/L	<70	<70	<70	0	0
Selenium, Se	Excess stillage	ug/L	<20	<20	<20	0	0
Silver, Ag (Det Lim.=1)	Excess stillage	ug/L	1.8	1.2	1.5	0.85	57
Thallium, Tl	Excess stillage	ug/L	<10	<10	<10	0	0
Titanium, Ti	Excess stillage	ug/L	1,300	1,300	1,300	0	0
Zinc, Zn	Excess stillage	ug/L	2,800	3,000	2,900	280	9.8

$\bar{X}$ = Average value
S = Standard deviation

TABLE A-2. ACURACY ASSESSMENT -- INORGANICS ANALYSES

Parameter	Sample	Sample concentration	Units	Spiking level (adjusted for dilution)	Recovery, percent ^a
Sugars	Fermenter (warm)	0.04	% wt/v	0.2	105
BOD	Chopper product	47,000	mg/L	40,000	115
COD	Thin stillage	54,800	mg/L	50,000	93
Phenols	Excess stillage	225	µg/L	1,000	100
Cyanide	Excess stillage	40	µg/L	112	95
Sulfate	Excess stillage	2,400	mg/L	2,000	108
Nitrate	Excess stillage	2.7	mg/kg	5.0	86
Ammonia	Excess stillage	270	mg/L	500	101
Kjeldahl nitrogen	Excess stillage	2,110	mg/L	5,000	104
Phosphorus	Excess stillage	340	mg/L	500	94
Aluminum	Excess stillage	22,300	µg/L	40,000	83
Antimony	Excess stillage	<20	µg/L	100	38
Arsenic	Excess stillage	<20	µg/L	200	70
Barium	Excess stillage	430	µg/L	1,000	107
Beryllium	Excess stillage	1.7	µg/L	10	75
Bismuth	Excess stillage	<200	µg/L	2,400	73
Cadmium	Excess stillage	8.5	µg/L	20	100
Calcium	Excess stillage	140,000	µg/L	200,000	114
Chromium	Excess stillage	125	µg/L	200	109
Copper	Excess stillage	1,500	µg/L	4,000	105
Iron	Excess stillage	29,500	µg/L	80,000	106
Lead	Excess stillage	16	µg/L	100	116
Magnesium	Excess stillage	176,000	µg/L	100,000	94
Manganese	Excess stillage	1,500	µg/L	4,000	108
Mercury	Excess stillage	7	µg/L	100	75
Nickel	Excess stillage	<70	µg/L	1,000	100
Selenium	Excess stillage	<20	µg/L	200	64
Silver	Excess stillage	1.5	µg/L	10	91
Thallium	Excess stillage	<10	µg/L	100	35
Titanium	Excess stillage	1,300	µg/L	2,000	100
Zinc	Excess stillage	2,900	µg/L	8,000	108

^aRecovery = $\frac{\text{Spiked Sample Result} - \text{Sample Result}}{\text{Spiking Level}} \times 100$ percent

TABLE A-3. ACCURACY ASSESSMENT -- ORGANICS ANALYSES

Parameter	Excess Stillage		Method Standard	
	Spiking Level µg/50 ml	Recovery, percent ^a	Spiking Level µg/L	Recovery, percent ^a
<u>Acid Surrogates:</u>				
d ₅ -phenol	100	93	100	109
d ₄ -2-nitrophenol	100	51	100	109
<u>B/N Surrogates:</u>				
d ₅ -nitrobenzene	100	17	100	116
d ₈ -naphthalene	100	70	100	73
d ₁₂ -chrysene	100	59	100	119
<u>Acid Spike:</u>				
p-chloro-m-cresol	100	72	100	130
2-chlorophenol	100	40	100	100
4-nitrophenol	100	110	100	123
pentachlorophenol	100	89	100	146
phenol	100	48	100	100
<u>B/N Spike:</u>				
Acenaphthylene	100	44	100	82
1,2,4-trichlorobenzene	100	110	100	130
1,4-dichlorobenzene	100	98	100	110
di-N-butylphthalate	100	22	100	65
pyrene	100	72	100	84
acenaphthene	100	67	100	98
chrysene	100	44	100	95

$$^a\text{Recovery} = \frac{\text{Spiked Sample Result} - \text{Sample Result}}{\text{Spiking Level}} \times 100 \text{ percent}$$

TABLE A-4. EPA SUPPLIED PERFORMANCE SAMPLES

Parameter	Analyst ^a	Analysis ^b date	Method ^c code	Sample I.D.	Reported value	Acceptance limits	Warning limits	Performance evaluation
Nitrate	SG	4/7/82	27	1F	0.27 mg/l as N	0.203-0.296 mg/l	0.214-0.285 mg/l	Acceptable
Total Kjeldahl	JL	12/15/81	21	2F	0.25 mg/l as N	0.146-0.563 mg/l	0.199-0.511 mg/l	Acceptable
Total phosphorus	CM	1/7/82	22	2F	0.10 mg/l as P	0.066-0.129 mg/l	0.073-0.121 mg/l	Acceptable
pH	SG	12/9/81	21	1G	7.65	-----Not available; see sample 1C-----	-----	-----
Specific cond	SG	12/9/81	21	1G	143u mhos/cm	110-147u mhos	115-143u mhos	Acceptable
Calcium	CM	1/15/82	21	1G	4.00 mg/l	2.89-5.27 mg/l	3.19-4.95 mg/l	Acceptable
Magnesium	CM	1/15/82	21	1G	3.40 mg/l	2.62-4.25 mg/l	2.82-4.05 mg/l	Acceptable
Sulfate	SG	12/30/81	22	1G	15 mg/l as SO ₄ -2	10.6-18.7 mg/l	11.6-17.7 mg/l	Acceptable
Oil and greased	SG	1/8/82	99	1L	13 mg/l	13.4-27.4 mg/l	15.7-25.1 mg/l	Not acceptable
Oil and greased	SG	1/8/82	99	2L	26 mg/l	28.8-36.4 mg/l	30.1-35.1 mg/l	Not acceptable
Oil and greased	SG	3/19/82	99	#1	12.4 mg/l	9.6-15.8 mg/l	--	Acceptable
Oil and greased	SG	3/15/82	99	#2	18.8 mg/l	15.7-25.1	--	Acceptable
pH	SG	12/9/81	21	1C	8.13	7.86-8.41	7.93-8.34	Acceptable
TSS	SG	12/10/81	99	1D	32 mg/l	21.9-36.3 mg/l	24.3-33.9 mg/l	Acceptable
TOC	BC	12/22/81	99	1E	85 mg/l	64.5-106 mg/l	69.8-101 mg/l	Acceptable
COD	SG	1/11/82	21	1E	202 mg/l	182-244 mg/l	189-237 mg/l	Acceptable
BOD	SG	12/9/81	99	1E	65 mg/l	63.5-138 mg/l	72.6-129 mg/l	Check for error
TOC	BC	12/22/81	99	2E	6.5 mg/l	2.65-10.8 mg/l	4.0-9.4 mg/l	Acceptable
COD	SG	1/8/82	21	2E	14.9 mg/l	1.87-27.8 mg/l	6.2-23.5 mg/l	Acceptable
BOD	SG	12/9/81	99	2E	3.0 mg/l	0.0-6.12 mg/l	1.0-5.1 mg/l	Acceptable
Cyanide	CM	12/17/81	99	1B	0.06 mg/l	0.050-0.096 mg/l	0.055-0.091 mg/l	Acceptable

^aAnalyst: SG (S. Guinnane);
 JL (J. Labash);
 CM (C. McMillen);
 BC (Brown & Caldwell, subcontractor)

^bRepeat samples for oil and grease were performed in April

^cFor method code 99 procedure see body of report

^dFor discussion of oil and grease results see body of report

(continued)

TABLE A-4. EPA SUPPLIED PERFORMANCE SAMPLES (Concluded)

Parameter	Analyst ^a	Analysis date	Method ^b code	Sample I.D.	Reported Value	Acceptance limits	Warning limits	Performance evaluation
Arsenic	CM	1/8/82	99	2A	20 µg/l	16.4-29.7 µg/l	18.6-27.5 µg/l	Acceptable
Barium	CM	1/14/82	99	2A	150 µg/l	87.9-222 µg/l	110-200 µg/l	Acceptable
Cadmium	CM	1/7/82	99	2A	2.6 µg/l	1.16-4.77 µg/l	1.78-4.17 µg/l	Acceptable
Chromium	CM	1/6/82	99	2A	15 µg/l	6.26-15.9 µg/l	7.86-14.3 µg/l	Check for error
Copper	CM	1/6/82	99	2A	<5 µg/l	-----Not present-----	-----	Acceptable
Iron	CM	1/14/82	99	2A	<30 µg/l	-----Not present-----	-----	Acceptable
Mercury	CM	1/13/82	99	2A	1.3 µg/l	0.253-2.47 µg/l	0.622-2.10 µg/l	Acceptable
Lead	CM	1/6/82	99	2A	24 µg/l	12.1-35.0 µg/l	15.9-31.2 µg/l	Acceptable
Selenium	CM	1/11/82	99	2A	6 µg/l	1.59-9.71 µg/l	2.94-8.36 µg/l	Acceptable
Silver	CM	1/7/82	99	2A	26 µg/l	12.3-35.1 µg/l	12.3-35.1 µg/l	Acceptable
Aluminum	CM	1/15/82	99	1A	460 µg/l	359-641 µg/l	394-606 µg/l	Acceptable
Arsenic	CM	1/8/82	99	1A	114 µg/l	73.6-164 µg/l	84.8-152 µg/l	Acceptable
Beryllium	CM	1/15/82	99	1A	450 µg/l	392-549 µg/l	412-529 µg/l	Acceptable
Cadmium	CM	1/7/82	99	1A	25 µg/l	22.7-36.5 µg/l	24.4-34.8 µg/l	Acceptable
Chromium	CM	1/6/82	99	1A	93 µg/l	53.8-96.2 µg/l	59.0-91.0 µg/l	Check for error
Copper	CM	1/6/82	99	1A	126 µg/l	106-152 µg/l	111-146 µg/l	Acceptable
Iron	CM	1/14/82	99	1A	260 µg/l	222-330 µg/l	235-317 µg/l	Acceptable
Lead	CM	1/6/82	99	1A	190 µg/l	167-252 µg/l	177-242 µg/l	Acceptable
Manganese	CM	1/14/82	99	1A	180.8 µg/l	152-225 µg/l	161-216 µg/l	Acceptable
Mercury	CM	1/13/82	99	1A	5.8 µg/l	4.08-8.22 µg/l	4.61-7.69 µg/l	Acceptable
Nickel	CM	1/15/82	99	1A	130 µg/l	114-181 µg/l	122-173 µg/l	Acceptable
Selenium	CM	1/11/82	99	1A	37 µg/l	17.8-48.3 µg/l	21.7-44.5 µg/l	Acceptable
Zinc	CM	1/14/82	99	1A	120 µg/l	115-164 µg/l	121-158 µg/l	Check for error

^aAnalyst: CM (C. McMillen)

(concluded)

^bFor method code 99 procedure see body of report